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## Hydrothermal synthesis and magnetic behaviour of $\beta$ - $\text{Li}_3\text{VF}_6$ and $\text{Na}_3\text{VF}_6$

Lei Ge,<sup>a</sup> Long Yuan,<sup>a</sup> Keke Huang,<sup>a</sup> Wenchun Feng,<sup>b</sup> Hairui Fang<sup>a</sup> and Shouhua Feng<sup>\*a</sup>

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**Fluorides and oxide-fluorides play important roles in several technological fields. Herein, we have synthesized the crystals of  $\beta$ - $\text{Li}_3\text{VF}_6$  and  $\text{Na}_3\text{VF}_6$  under mild hydrothermal conditions without any hydrofluoric acid. These two compounds were well-crystallized and showed anti-ferromagnetic interactions with isolated magnetic units.**

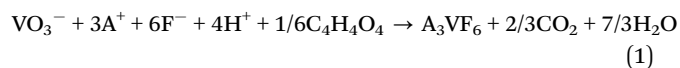
Fluorides and oxide-fluorides have significant importance in the development of many new technologies such as luminescence,<sup>1–3</sup> catalysis,<sup>4–6</sup> energy conversion and storage.<sup>7–9</sup> Most of these applications are impacting various key points of modern life and are irreplaceable. Therefore, developing more secure and efficient synthetic strategies is a priority.

Many methods have been applied to the preparation of fluorides such as solid-state reactions,<sup>10–12</sup> sol-gel precursors,<sup>13–16</sup> flux growth,<sup>17,18</sup> hydrothermal/solvothermal processing<sup>19–24</sup> and a molten-salt electrolysis method.<sup>25</sup> Among these methods, hydrothermal or solvothermal process provides an attractive synthetic route for the synthesis of a meta-stable phase or materials with numerous advantages, such as low growth temperature, one-step synthesis procedure, easy handling and controllable particle size distribution.<sup>26,27</sup> Under mild hydrothermal conditions, complex fluorides, such as perovskite-type fluorides ( $\text{LiBaF}_3$  and  $\text{KMgF}_3$ ), the scheelite-type fluorides ( $\text{LiYF}_4$ ,  $\text{NaYF}_4$ ,  $\text{KYF}_4$ ,  $\text{KMgF}_4$ ) and double perovskite vanadium fluorides ( $(\text{NH}_4)_2\text{NaVF}_6$  and  $\text{Na}_3\text{VF}_6$ ),<sup>28–30</sup> have been synthesised by our group.

However, the traditional fluoride hydrothermal process involves an excessive use of HF acid, which results in the presence of an extreme stoichiometric excess of  $\text{F}^-$  ions.<sup>24,30</sup> Due to the HF being both highly corrosive and toxic, the operator should be well trained and protected during the entire process. After the reaction, the unreacted surplus  $\text{F}^-$  ions are left in Teflon-lined autoclaves,

which increases the risk for the operator and creates difficulties during the treatment of waste liquid by-products. Taking an example of a traditional  $\text{Na}_3\text{VF}_6$  hydrothermal process,<sup>30</sup> for a yield of up to 100%, at least 41 mmol  $\text{F}^-$  ions are present for every 1 mmol of product obtained due to the massive addition of 2 mL of HF acid. The health risks for  $\text{F}^-$  ions in water include chronic toxic effects on teeth, food intake, bones and soft tissues.<sup>31–34</sup>

HF acid as a common mineralizer are widely used in many fluoride and oxide-fluoride hydrothermal synthesis processes, which plays an important role in the promotion of dissolution, crystal nucleation and phase growth.<sup>28,29,35–37</sup> Thus, it is nearly impossible to remove or even to reduce the dosage of HF acid in traditional hydrothermal synthesis routes. To solve this problem, two methods can be considered: (i) to find a mineralizer substitute to HF acid and (ii) to adopt a new chemical reaction to overcome the limitations in traditional experiments. Herein, we present a reduction reaction of V ions from +5 to +3 with (*E*)-2-butenedioic acid ( $\text{C}_4\text{H}_4\text{O}_4$ ) to reach our goal (eqn (1)) without the addition of HF acid. The goal was to provide information towards a more green hydrothermal fluorine chemistry with lower  $\text{F}^-$  ion residue. X-ray photoelectron spectroscopy (XPS) showed that  $\text{V}^{5+}$  was reduced to  $\text{V}^{3+}$  during the synthesis process. A temperature-dependent magnetization study indicates antiferromagnetic interactions in both the samples.



The room-temperature powder XRD pattern of  $\beta$ - $\text{Li}_3\text{VF}_6$  is shown in Fig. 1a, which is well indexed in a monoclinic unit cell of the space group  $C2/c$  (ICDD-PDF 83-1433), while the  $\text{Na}_3\text{VF}_6$  room-temperature powder XRD pattern is well indexed in a monoclinic unit cell of space group  $P2_1/n$  (ICDD-PDF 29-1286), as shown in Fig. 1b. Fig. 2a and b show the schematic crystal structures of  $\beta$ - $\text{Li}_3\text{VF}_6$  and  $\text{Na}_3\text{VF}_6$ , respectively. In both the structures,  $\text{VF}_6$  units are separated from each other with  $\text{Li}^+$  or  $\text{Na}^+$  inserted between the neighbouring  $\text{VF}_6$  octahedrals.

<sup>a</sup> State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China. E-mail: shfeng@mail.jlu.edu.cn; Fax: +86-431-85168624; Tel: +86-431-85168661

<sup>b</sup> Department of Chemical Engineering, University of Michigan, Ann Arbor 48109, USA

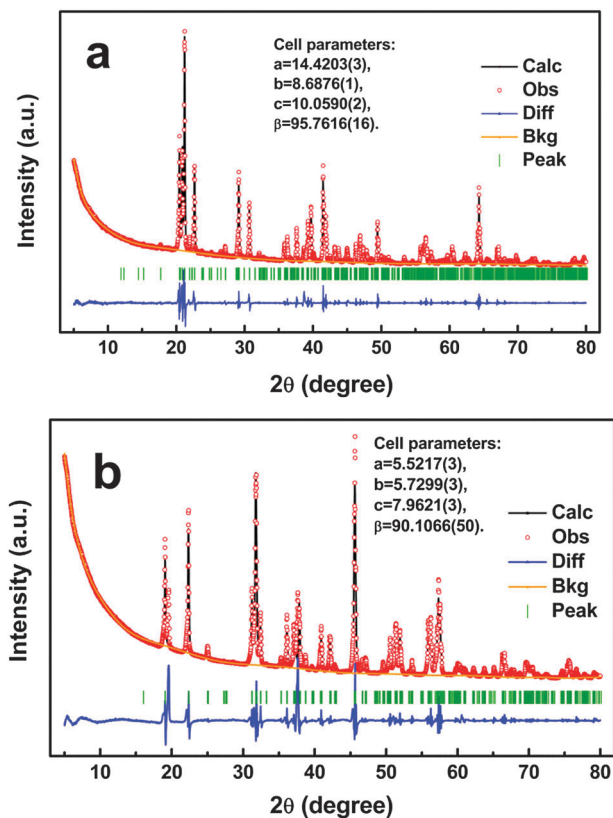


Fig. 1 X-ray diffraction patterns and Pawley refinement result of cell parameters of  $\beta\text{-Li}_3\text{VF}_6$  (a) and  $\text{Na}_3\text{VF}_6$  (b).

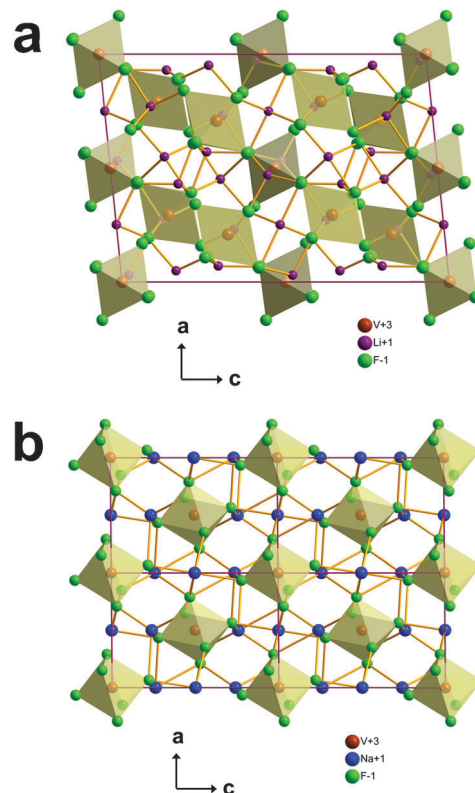


Fig. 2 Schematic of crystal structures (view along  $b$  axis) for  $\beta\text{-Li}_3\text{VF}_6$  (a) and  $\text{Na}_3\text{VF}_6$  (b), respectively.

The SEM images of the as-prepared compounds  $\beta\text{-Li}_3\text{VF}_6$  and  $\text{Na}_3\text{VF}_6$  are shown in Fig. 3. Both the compounds were well-crystallized with definite shapes and exposed facets of the final products. The shape of  $\beta\text{-Li}_3\text{VF}_6$  crystals mainly appear as twin-grown hexagonal prisms with pyramids at each tip. The crystal sizes were 100 to 200  $\mu\text{m}$  (Fig. 2a), which appear to be a little smaller than those previously reported by a microwave solvothermal process (*ca.* 400  $\mu\text{m}$ ),<sup>42</sup> while in the reported 1 : 3 water to ethanol ratio reaction process, spherical raspberry-like agglomerates with a size of *ca.* 450 nm were obtained.<sup>24</sup> The  $\text{Na}_3\text{VF}_6$  crystal is found to have a *ca.* 200  $\mu\text{m}$  octahedron form (Fig. 2b), which is larger than the  $\text{Na}_3\text{VF}_6$  previously synthesised by He *et al.* (*ca.* 100  $\mu\text{m}$ ) with a shape of a regular polyhedron.<sup>30</sup>

Surface charging has been shown in  $\text{Na}_3\text{VF}_6$  crystals (bright areas on the crystal surface) by obtaining SEM images with an accelerating voltage of only 5 kV and electron dosage below 21 pA. This result may indicate a poorer electronic conductivity for  $\text{Na}_3\text{VF}_6$  crystals than that of  $\beta\text{-Li}_3\text{VF}_6$ .

During the preparation process, pH value played an important role in the crystallization process. Both the products can be prepared in a weakly acidic environment. In the synthesis process of  $\text{Na}_3\text{VF}_6$ , all the reagents can afford sufficient amount of  $\text{H}^+$  to drive the reaction. No more acid was needed. However, for the synthesis of  $\beta\text{-Li}_3\text{VF}_6$ , the pH value was required to be adjusted to 4–6 to carry out the process. But, the precipitation dissolution equilibrium will be gradually destroyed with the

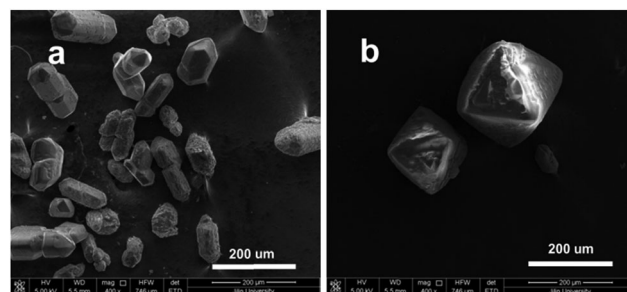


Fig. 3 SEM images of as-prepared  $\beta\text{-Li}_3\text{VF}_6$  (a) and  $\text{Na}_3\text{VF}_6$  (b) crystals.

increase of  $\text{H}^+$  ions. When the pH value was less than 3, no crystallization reaction occurred, and only a green solution containing  $\text{Li}^+$  (or  $\text{Na}^+$ ),  $\text{V}^{3+}$ ,  $\text{F}^-$ , and  $\text{NH}_4^+$  ions was obtained. When the reaction environment was basic,  $\text{LiF}$  and  $\text{Na}_2\text{VF}_5\text{O}$  impurities were detected.

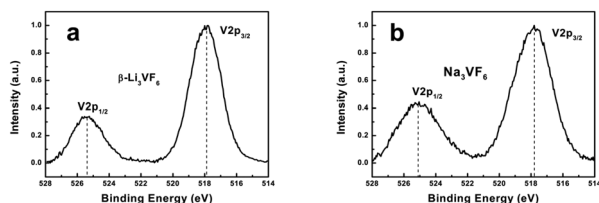
The reaction temperature also played an important role in the formation and crystallinity of the compounds. Impurities could be detected when the reaction temperature was lower than 240  $^\circ\text{C}$ .

To compare the residual  $\text{F}^-$  ions in this work with a reference,<sup>30</sup> we made a list for the requisite amount of  $\text{F}^-$  ions required to react with 1 mmol V and the residual  $\text{F}^-$  amount in the preparation process (Table 1).

X-ray photoelectron (XPS) spectra of  $\beta\text{-Li}_3\text{VF}_6$  and  $\text{Na}_3\text{VF}_6$  are shown in Fig. 4. No splitting of  $\text{V}2\text{p}_{3/2}$  peak is observed.

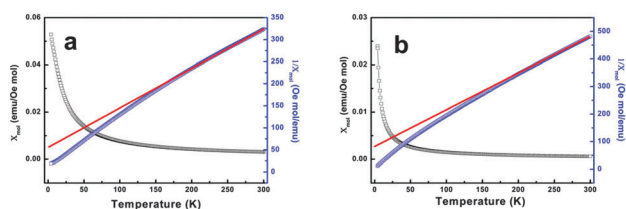
**Table 1** The difference in the amount of residual F<sup>-</sup> ions against the reference

Synthesis route	Source	Amount (mmol)	Total (mmol)	Residue (mmol)
Ref. 30	NaF	3	47	42.5
	HF acid	44		
This work	NH <sub>4</sub> HF <sub>2</sub>	6	6	1.7
Difference			41	40.8

**Fig. 4** XPS spectra of V2p for  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> (a) and Na<sub>3</sub>VF<sub>6</sub> (b).

Both the compounds exhibit the same V2p<sub>3/2</sub> peak at 517.8 eV. This indicates that the element V in these two compounds existed in the same oxidation state. From the molecular formula, we can infer that the oxidation state is +3. We can find that most of the oxides that contain V<sup>3+</sup> present the V2p<sub>3/2</sub> peak section in the range of 514.1–517.2 eV,<sup>38,39</sup> which is lower than the value of 517.8 eV. This phenomenon is mainly due to the coordination environment of V<sup>3+</sup>. Because F has a higher electronegativity than O, the V element will reflect a higher binding energy when it is coordinated with F<sup>-</sup> rather than with O<sup>2-</sup>. A similar phenomenon can also be found in CuBr<sub>2</sub>–CuCl<sub>2</sub>–CuF<sub>2</sub> series. With the increase of electronegativity from Br to F, the binding energy showed a same shift, which was about 4 eV higher.<sup>40,41</sup> Thus, the V2p<sub>3/2</sub> peak of these two compounds at 517.8 eV is reliable.

The molar magnetic susceptibilities,  $\chi_m$ , of  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> and Na<sub>3</sub>VF<sub>6</sub> were investigated in the temperature range from 4 K to 300 K with the heating rate at 4 K min<sup>-1</sup> and an applied field of 5 kOe, and are shown in Fig. 5; moreover, the plots of  $\chi_m^{-1}$  versus  $T$  are also listed in Fig. 5. The compounds show the existence of antiferromagnetic interactions. At a higher temperature range, their magnetic behaviour obeys the Curie–Weiss law  $\chi = C/(T - \theta)$  with  $C = 1.165$  cm<sup>3</sup> K mol<sup>-1</sup>,  $\theta = -68$  K for  $\beta$ -Li<sub>3</sub>VF<sub>6</sub>, and  $C = 0.7502$  cm<sup>3</sup> K mol<sup>-1</sup>,  $\theta = -62$  K for Na<sub>3</sub>VF<sub>6</sub>. The magnetic properties of  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> have not been reported previously, and the effective moment,  $\mu_{\text{eff}}$ , for compound  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> was calculated

**Fig. 5** The magnetization curves of  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> (a) and Na<sub>3</sub>VF<sub>6</sub> (b) in an applied field of 5 kOe.

to be  $2.76 \mu_{\text{eff}}/\mu_{\text{B}}$  by fitting the plot of  $\chi_m^{-1}$  versus  $T$  at a higher temperature zone, which is very close to the value of the spin-only state V<sup>3+</sup> ( $2.828 \mu_{\text{eff}}/\mu_{\text{B}}$ ). However, for Na<sub>3</sub>VF<sub>6</sub>,  $\mu_{\text{eff}}$  was  $2.23 \mu_{\text{B}}$ , which appears to be slightly lower than the value of the spin-only state V<sup>3+</sup> at room temperature. This phenomenon was explained by an antiferromagnetism super-exchange model observed in VF<sub>3</sub> at 18 K by Alter *et al.*<sup>43</sup> This value is still lower than  $2.573 \mu_{\text{B}}$ , which has been previously reported by He *et al.* (ICDD-PDF 26-1493). We suggest that the slightly different angle of V–F–Na bond maybe the reason for the lower value. Because the mechanism of the super-exchange interaction between the transition metals *via* fluorine is changed, the magnetic properties can be considered to be dramatically changed by the V–F–Na bond.<sup>30</sup>

In summary, by a reduction reaction, we have successfully synthesized  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> and Na<sub>3</sub>VF<sub>6</sub> in a mild hydrothermal environment without the use of hydrofluoric acid.  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> and Na<sub>3</sub>VF<sub>6</sub> were characterized by X-ray diffraction and X-ray photoelectron spectroscopy. The presence of a weakly acidic environment and (*E*)-2-butenedioic acid were the two key points for their synthesis. The compounds showed the existence of antiferromagnetic interactions.

## Experimental

All the reagents were used as received. Single crystals of  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> and Na<sub>3</sub>VF<sub>6</sub> were synthesized from a mixture of NH<sub>4</sub>VO<sub>3</sub>, NH<sub>4</sub>HF<sub>2</sub>, LiCl (or NaCl), (*E*)-2-butenedioic acid and deionized water. After heating in a water bath with magnetic stirring for about 10 min at 80 °C, the pH was adjusted to 4–6 with hydrochloric acid. Then, the mixture was transferred to a 15 mL Teflon-lined stainless-steel autoclave, which was filled to about 80% of its capacity. The autoclave was heated to 240 °C for 24 h and cooled to room temperature naturally. Then, the crystalline products were washed with deionized water and ethanol to dislodge water-soluble impurities and organic molecules. Finally, the products were dried in air at ambient temperature. Besides (*E*)-2-butenedioic acid, all the reagents were added in a stoichiometric ratio, with 0.254 g LiCl, 0.234 g NH<sub>4</sub>VO<sub>3</sub>, 0.342 g NH<sub>4</sub>HF<sub>2</sub>, 0.07 g (*E*)-2-butenedioic for  $\beta$ -Li<sub>3</sub>VF<sub>6</sub> synthesis process and 0.254 g 0.352 g NaCl, 0.234 g NH<sub>4</sub>VO<sub>3</sub>, 0.342 g NH<sub>4</sub>HF<sub>2</sub>, 0.07 g (*E*)-2-butenedioic for Na<sub>3</sub>VF<sub>6</sub> synthesis process.

Product composition was determined by powder X-ray diffraction (XRD) data, which were collected on a Rigaku D/Max 2500V/PC X-ray diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.54718$  Å) at 50 kV and 200 mA with a scan speed of 1° min<sup>-1</sup> at room temperature. The step scanning was in the angle range of  $5^\circ \leq 2\theta \leq 80^\circ$  with an increment of 0.02°. Scanning electron microscope (SEM) images were obtained with a Helios NanoLab 600i dual beam system, FEI Company, America. *M*–*T* magnetization measurements were performed on an MPMS (SQUID) VSM, Quantum Design, America. The measuring temperature range was from 4 to 300 K, and the applied field was 5 kOe. XPS spectra were acquired with a Thermo Scientific ESCALAB 250 X-ray photoelectron spectrometer (XPS) Microprobe, America.

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